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Edge-on Lamellae of Polyoxymethylene Crystallized from Solutions Epitaxially onto Alkali Halides

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Edge-on crystalline lamellae of polyoxymethylene (POM) were isothermally grown onto the (001) face of NaCl or KCl from 0.1 wt% solutions (solvent: nitrobenzene, acetophenone, benzyl alcohol, *m*-cresol). The thickness of crystalline core in the edge-on lamella increased with decreasing supercooling (ΔT), but was inevitably smaller than the corresponding lamellar thickness for any ΔT . Accordingly, the POM edge-on lamella should have a surface layer (20–25% of the lamellar thickness) containing folds on each side of its crystalline core.

Keywords : POM/ Epitaxy/ Transmission electron microscopy/ TEM/ Electron diffraction/ Dark-field image/ Lamellar thickness/ Crystalline core

Epitaxy of polyoxymethylene (POM) onto various alkali halides has been studied extensively [1-6]. In analogy with polyethylene (PE) [7], typical morphology of POM on the (001) face of an alkali halide observed by transmission electron microscopy (TEM) is characterized by rodlike crystals oriented in the $\langle 110 \rangle$ directions of the substrate. Electron diffraction (ED) revealed that the chain stems in such rodlike crystals lie parallel to the substrate surface and are also oriented in the $\langle 110 \rangle$ directions of the substrate [4,5]. Recently, it was proposed that the chain stems in the rodlike crystal of POM grown epitaxially on NaCl might be set parallel to the long axis of the rod with a triangular cross-section [6]. Before this proposal, it had been postulated that the stems in the rod should be packed perpendicular to its long axis, *i.e.*, each of the rodlike crystals of POM had been regarded as an "edge-on" lamella [5], without any conclusive evidences. Here, we will report the morphology of the rodlike crystals of POM grown on alkali halides which was studied by TEM in bright- and dark-field imaging modes, and also will discuss the dependence of the crystalline-

core thickness on the crystallization temperature (T_c).

POM (TENAC 5010, $M \approx 40,000$; Asahi Chemical Industry Co., Ltd.) was utilized. Substrates used here were NaCl and KCl, the (001) faces of which were freshly cleaved just before use, because only the hexagonal form of POM is expected to grow on both of them [4]. Nitrobenzene, acetophenone, benzyl alcohol, and *m*-cresol were used as a solvent. At desired T_c 's, epitaxy was performed isothermally ($T_c \pm 1^\circ\text{C}$) for 60 seconds in every 0.1 wt% solution of POM under an N_2 atmosphere. TEM was carried out with a JEOL JEM-200CS operated at 160 or 200 kV. For ED and dark-field imaging, a specimen-rotating holder was utilized.

On both of the substrates, the rodlike crystals were surely oriented in the $[110]$ and $[-110]$ directions of the substrate, being perpendicular to each other [8, 9]. By ED experiments, the crystal form of the rodlike crystals of POM grown on NaCl and KCl was confirmed to be hexagonal (9/5 helix: $a = 0.447$ nm, c (chain axis) = 1.739 nm) [10]. Evidently, the crystals on KCl were nucleated much more densely than those on NaCl, prob-

STATES AND STRUCTURES — Polymer Condensed States —

Scope of research

Attempts have been made to elucidate the molecular arrangement and the mechanism of structural formation/change in crystalline polymer solids, polymer gels and elastomers, polymer liquid crystals, and polymer composites, mainly by electron microscopy and/or X-ray diffraction/scattering. The major subjects are: synthesis and structural analysis of polymer composite materials, preparation and characterization of polymer gels and elastomeric materials, structural analysis of crystalline polymer solids by direct observation at molecular level resolution, and in situ studies on structural formation/change in crystalline polymer solids.



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ably because KCl has a nearly perfect lattice-matching with the hexagonal POM than other alkali halides [4]. In contrast, nucleation took place less frequently on NaCl, and accordingly, most of the resulting rodlike crystals could grow much longer.

It was not easy to measure correctly the width of rodlike crystal. Occasionally, however, we could do so for some crystals giving adequate mass-thickness contrast only in the bright-field image of Pt-Pd-shadowed rodlike crystals grown on KCl at 125°C. In this case, the average width of the rodlike crystals was estimated at 9.1 (± 1.7) nm. This value is approximately compatible with the lamellar thickness measured before by small-angle X-ray scattering (SAXS) of single crystal mats [11,12], as shown in Fig.1.

In the ED patterns obtained here, two *hhl* net-patterns of the hexagonal lattice, which are perpendicular to each other, were recognized. Therefore, it can be concluded that the chain axis in the rodlike crystal is oriented in either [110] or [-110] direction of the substrates and the contact plane of the rodlike crystal, *viz.* the plane in contact with the substrate surface is the (100) plane of hexagonal POM [8,9]. In order to determine the direction of chain axis in the rodlike crystals, the 100 dark-field image of them was taken after tilting the specimen by $|30^\circ|$ around the axis perpendicular to the long axis of the rod [8]. From the image, it was determined that POM chain stems are set perpendicular to the long axis of the rodlike crystal, strictly speaking, to that of the crystalline core in the rodlike crystal. These results definitely revealed that each of the rodlike crystals grown epitaxially on KCl and NaCl is an edge-on folded-chain lamella of POM, taking into account the lateral width of the crystals and the molecular weight of POM [8,9]. Each bright striation in the dark-field image, therefore, corresponds to the crystalline core in the edge-on lamella [7-9]. Using the present dark-field imaging technique by TEM, we can directly estimate the crystalline-core thickness, *viz.* the stem length in an edge-on lamella. For this purpose, KCl was used as a substrate.

It is well known that the lamellar thickness increases approximately linearly with increasing reciprocal of the supercooling, $1/\Delta T$ [12]. Here, $\Delta T \equiv T_d^0 - T_c$, where T_d^0 is the equilibrium dissolution temperature for each solvent. The values of T_d^0 and of the lamellar thickness of POM single crystals grown isothermally at various T_c 's were quoted from literature [11] for each solvent used in this report.

Figure 1 shows the $1/\Delta T$ -dependence of the crystalline-core thickness, which was obtained by the dark-field TEM [9], and also that of the lamellar thickness of single crystals grown from solutions, which was estimated by SAXS [11,12]. Obviously, the crystalline-core thickness is smaller than the corresponding lamellar thickness and is about half the lamellar thickness at any $1/\Delta T$, though it increases with increasing $1/\Delta T$. Accordingly, the POM edge-on lamella should have a surface layer (20~25% of the lamellar thickness) containing folds on each side of its crystalline core: the layer is presumed to be composed of adjacent-reentrant folds with some fluctuation in contour

length and its resultant fluctuation in conformation as in the solution-grown lamellae of PE [7], by taking into account the results of surface decoration [9,13] and atomic force microscopy [14] of the POM single crystals.

From only the present results, however, it was difficult to determine whether the crystalline-core thickness increases linearly with $1/\Delta T$ or not, though in our temperature range in Fig.1 the lamellar thickness increases fairly linearly with increasing $1/\Delta T$ [12]. For more accurate estimation of crystalline-core thickness, lattice imaging by high-resolution TEM (HRTEM) seems to be the best method. It is, however, difficult to take an HRTEM image of the edge-on lamellae of POM, because they are vulnerable to electron irradiation and in addition their orientation is not appropriate. HRTEM studies on other polymers, which are less sensitive against electron irradiation and have adequate crystallite orientation, are in progress [15].

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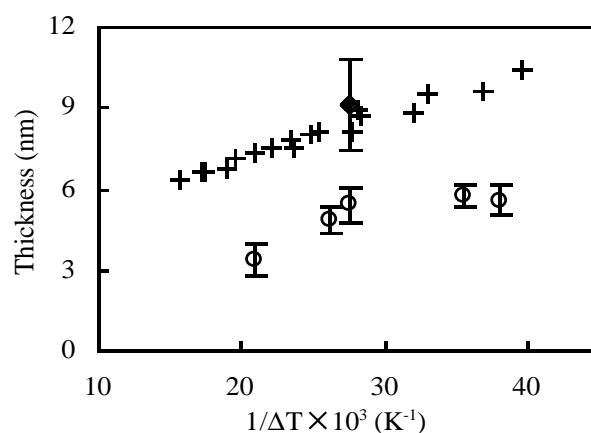


Figure 1. Crystalline-core thickness (o) and lamellar thickness (+, ♦) plotted against the reciprocal of the supercooling (ΔT). The values of lamellar thickness (+), which were measured by SAXS, were quoted from ref 11, and that (♦) was estimated by bright-field TEM. The vertical bars represent standard deviations.